AN APPLIED METHOD FOR CADMIUM ANALYSIS OF RICE BY COLORIMETRIC MICRODETERMINATION WITH DITHIZONE

Masumi MORITSUGU

In a previous paper, the results of experiments on the cadmium content of rice were reported (Moritsugu and Kobayashi 1964). A suitable analytical procedure of cadmium for rice samples was additionally presented there.

In the present paper, the improved process of ashing for rice samples and an applicability of colorimetric microdetermination of cadmium with dithizone for rice samples are described in detail.

Although care must be taken to prevent the volatilization of cadmium at high temperature, dry ashing methods are preferable for a rapid preparation of a large number of organic samples. The dry ashing procedure described here is sufficiently applicable for rice samples without significant loss of cadmium, provided that furnace temperature is controlled strictly and sodium sulfate is used as an ashing aid.

Among many methods of colorimetric microdetermination of cadmium with dithizone (Snell and Snell 1949, Saltzman 1954, Sandel 1959, A. O. A. C. 1960), the method of Saltzman is most preferable from the view points of sensitivity, recovery, specificity, simplicity and color stability. But, his method has a weak point for rice samples. The analytical results obtained by this method are liable to lower whenever the strong alkaline aqueous layer turns red at the end of the first extraction stage. It is confirmed that these interferences are brought about by the presence of a considerable amount of magnesium and a small amount of common metals such as zinc and lead. The improved method described here is well applicable for the rice samples by the sufficient addition of sodium-potassium tartrate to the neutralized sample solution at the beginning of the first extraction, although the sample contains such an abundance of magnesium as the ratio of magnesium to cadmium reaches more than 10, 000.

REAGENTS AND APPARATUS

All the reagents used in this experiment are made from analytical grade chemicals. High-purity deionized water is used for the preparation of the reagents.

From the blank determination along with the determination on the samples, it is seen that all the reagents, except chloroform, and water give no effect upon the analytical results. Some analytical grade chloroform contains an impurity having oxidizing ability, and common interfering metals. However, these are

excluded by precautional treatment.

Methods of reagent make up are not described here because the methods are equal to that of Saltzman.

The main apparatus used in this experiment are as follows; an electric muffle furnace with an automatic temperature regulator, a recording millivoltmeter with copper-constantan thermoelectric couples, a shaking machine for separatory funnel, a photoelectric spectrophotometer of Beckman type, separatory funnels of Squibb type and some other glasswares.

RESULTS AND DISCUSSION

1. *Experiment on Ashing Method*

As to the ashing method for cadmium analysis of organic materials, it has been said that the dry ashing at 500°C gives low results (Snell and Snell). Wet ashing has been therefore recomended (Snell and Snell, Saltzman, Sandel, A. O. A. C.).

But, even 1 g of rice sample can not be decomposed by the mixture of concentrated sulfuric acid and nitric acid on account of severe foaming at the early stages of digestion. Needless to say, the digestion by only sulfuric acid is more difficult.

After all, a fairly avairable method is found out. The method consists in nitric acid digestion and decomposition by the mixture of nitric acid and perchloric acid (Snell and Snell). These procedures have been applied for the wet ashing of rice samples by Katakura and Hatanaka (1959).

But, when the samples used exceed 5 g, they can hardly be decomposed by this method on account of considerable foaming. For the complete digestion of more than 5 g of rice samples, the preliminary procedures of preparation, i. e. the carbonization of the sample by dry method at about 300°C of furnace temperature, and the use of sodium sulfate as an ashing aid (Saltzman) are essential.

Furthermore, wet ashing has the following week points: It is hardly applicable to the common rice samples when their cadmium content is not so high, because the approximate amount of sample decomposed at once is limited to less than 5 g. Care must be taken to the toxicity of acid fumes and contamination derived from acid used in a large amount. Additionally, continuous observation and gentle treatment are necessary to control acid volume and heating temperature during digestion. In conclusion the method is too troublesome.

From the above reasons, it is considered that the wet ashing is rather undesirable for a large number of samples which contain a very small amount of cadmium.

Meanwhile, in the case of dry ashing of rice samples at the furnace temperature of 500°C (the temperature was established by several workers, Snell and Snell, Sandel, Agr. Chem. Kyoto Univ. 1960, for the trace elements found in organic

samples.), the ashing is very difficult, because the carbon-free ash can not be obtained even by the ashing for a few days.

The carbon-free ash is easily obtained when the furnace temperature is elevated to about 650°C. But in this case, cadmium loss is significant. Moreover, the ash adheres to the bottom of the crucible and it is liable to become acid-insoluble when the ceramic crucible is used.

If the process of nitric acid moistening is made after the furnace ashing for a night, the carbon-free ash can be obtained within 500°C of furnace temperature.

Thus, the following experiments are made about ashing temperatures and ashing aids, in order to find the condition of dry ashing without any loss of cadmium.

Experiment on Ashing Temperature

The relation between ashing temperature and loss of cadmium was studied on rice samples. The results obtained was similar to those of Saino and Kobayashi (1963) on the same subject.

In addition to their findings, it is suggested that the cadmium loss at high temperatures is increased inversely to the sample weight in one crucible, and the cadmium loss is increased by the addition of ashing aid, especially when an alkaline chemicals is used (Fig. 1).

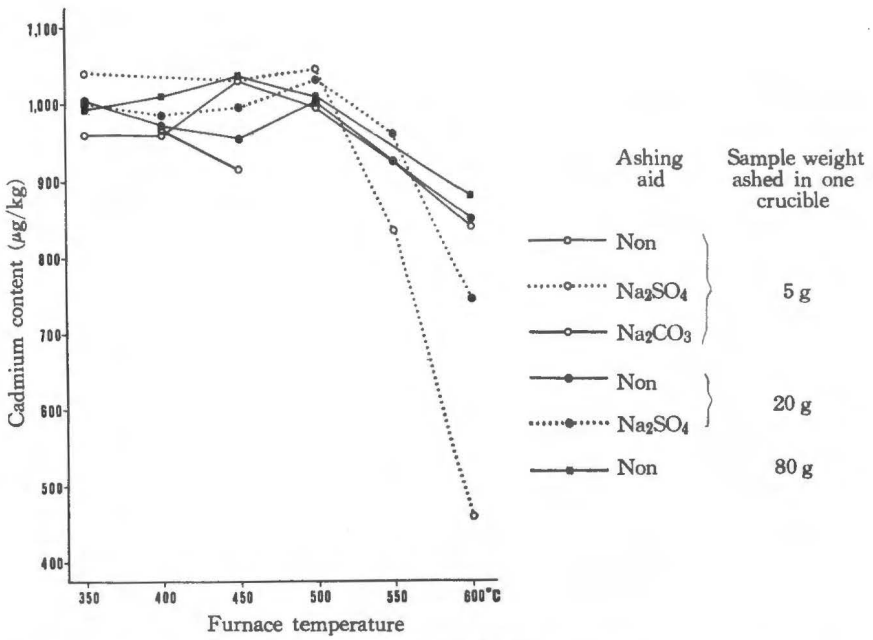

Fig. 1. Relation between ashing temperature and loss of cadmium
Rice sample is obtained from a mine-poisoned area in Toyama Prefecture.

In the present study, the continuous measurement of temperature is made on the rice samples through ashing process, in order to clarify the relation between the furnace temperature and the ashing sample temperature, and to estimate the sample temperature at the beginning of cadmium loss.

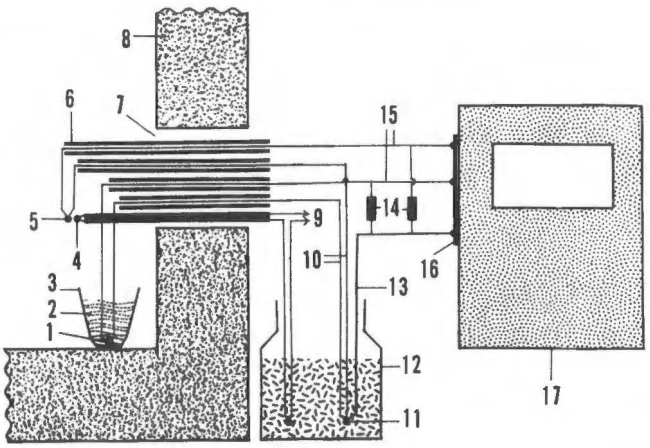

Fig. 2. Outlined arrangement of equipments for the temperature recording of ashing samples
1. Copper-constantan thermocouple for measurement of sample temperature.
2. Rice sample (20 g).
3. Ceramic crucible.
4. Chromel-alumel thermocouple for the automatic temperature regulation of furnace.
5. Copper-constantan thermocouple for temperature recording of furnace.
6. Glass tube (4 mm diameter).
7. Backside hole of furnace.
8. Adiathermanous wall of furnace.
9. To automatic temperature regulator of high frequency ossilation type.
10. Constantan wire (0.2 mm diameter).
11. Reference junction.
12. Ice box.
13. Copper wire (−side, stranded, coated with vinyl chloride).
14. Shunting resistance (10 Ω).
15. Copper wire (+side, 1 mm diameter).
16. Input terminal.
17. Rrecording millivoltmeter (10 mv full scale).

Small copper-constantan thermoelectric couples, brass soldered, are used for the temperature measurement of the furnace and the rice samples. The thermocouples are inserted into the bottom part of 20 g of the rice samples in several crucibles under different conditions. With a recording millivoltmeter, the thermoelectric voltages of several crucibles are continuously recorded. The voltages measured are transformed to the temperatures.

The results obtained are summarized in Fig. 3. The furnace temperature is set at 400°C in case of the chart (1) and at 450°C in case of the chart (2). And in both cases, temperature recording is made for 10 hours from the begining of

ashing. But, it is questioned whether the temperature of ashing samples shown in Fig. 3 is accurate throughout the measurement, because the thermocouple and the sample become severable from the initial close contact as the ashing proceeds. Accordingly, the sample temperature is doubtfull after its sudden fall.

From the results shown in Fig. 3, it is probable that the sample temperature in the early stages of ashing is higher than the furnace temperature. A remarkable difference between temperature of sample and furnace (Fig. 3-(2)) is seen in the

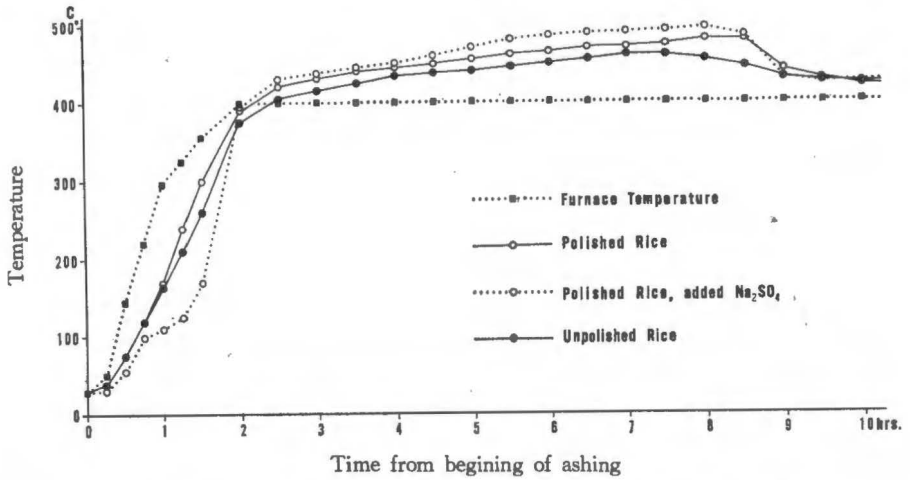

Fig. 3.-(1). Ashing sample temperature in early stages of ashing (Furnace temperature 400°C)

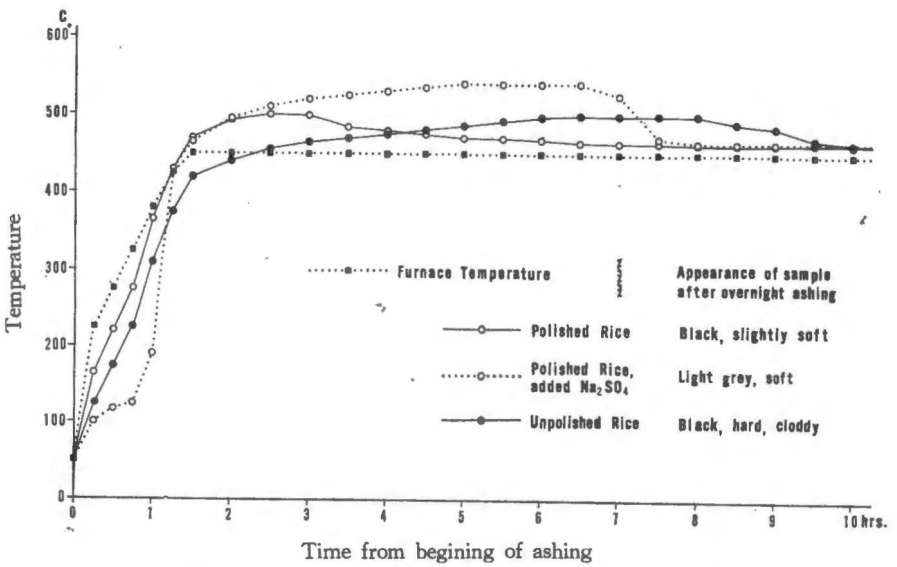

Fig. 3.-(2). Ashing sample temperature in early stages of ashing (Furnace temperature 450°C)

case of polished rice to which sodium sulfate is added as an ashing aid, the sample temperature being about 540°C in contrast to 450°C of the furnace temperature. On the contrary, less difference in the same chart is seen in cases of unpolished rice and polished rice to which ashing aid is not added, the temperature being approximately 500°C.

Hence, it is considered that the temperature elevation of ashing sample is affected by the composition of samples. (This is different among unpolished rice, polished rice, and those with and without ashing aid.) In addition, the temperature elevation brings about effect on the easiness of ashing as seen from Fig. 3-(2). Accordingly, it is suggested that the more easily the sample is ashed, the more remarkably its temperature is elevated.

From the above results, the maximum furnace temperature for rice ashing is at 450°C for the rice samples to which ashing aid is added, and bellow 500°C for the common rice samples to which that is not added.

Additionally, in case of dry ashing by a regular electric furnace, the furnace temperature of which is not regulated automatically, it is anxious about the temperature elevation of samples which may be more remarkable than in the case of this experiment in which the automatic temperature regulator is used, because the elevation of sample temperature must boost the furnace temperature and the elevated furnace temperature must act to boost the sample temperature, i. e. the temperature of furnace and samples is further elevated by their interaction. In this meaning, it is considered that the use of such a regular electric furnace is undesirable for the ashing of organic samples in the determination of the elements easily affected by high temperatures.

As for the relation between cadmium loss and sample temperature, it is considered that the cadmium loss begins at sample temperature a little over 600°C, because the temperature of ashing sample is rose higher by about 50°C or more than the furnace temperature (Fig. 3), and because the cadmium loss is observed from furnace temperature of 550°C as indicated in Fig. 1.

Experiment on Ashing Aid

Sometimes, ashing aid is used for the samples which are hardly decomposed by dry ashing. The ashing aid commonly used is as follows; magnesium nitrate, magnesium acetate, the mixture of aluminum nitrate and calcium nitrate, etc.

Among these chemicals, magnesium salts are undesirable for this colorimetric method, because magnesium is a factor of analytical error as described below. The chemicals which are alkalized by ignition are also undesirable by reason of the fact that cadmium is very liable to loss in alkaline ash, as can be considered from the result of Fig. 1. Moreover, in ashing at furnace temperature below 500°C, these chemicals are inefectural for obtaining the carbon-free rice ash.

For the above reasons, these chemicals are undesirable as the ashing aid for the rice samples in which cadmium is determined by this method.

Consequently, sodium sulfate is chosen and examined for its avairability. This substance was recomended by Saltzman for the wet digestion of the organic samples containing low minerals.

As can be considered from Fig. 3, one of the reason why the ashing is hastened by the addition of ashing aid is an elevation of sample temperature. And, the cadmium loss at high temperatures increases by the addition of this ashing aid as seen from Fig. 1. Moreover, the process of nitric acid moistening is essential for obtaining the carbon-free ash, even when the sulfate is used as an ashing aid.

In spite of the above weak points, it has the following advantages: The frequencies of the process of nitric acid moistening and the amount of nitric acid required are reduced by half. Additionally, the carbonized samples over-scattered by sudden boiling during sand bath heating is decreased, because a many and small foams, which rise at the bottom of the crucible, break gently by the addition of vitriolic radical.

For fear of a small loss of cadmium which may occur in rice samples of certain composition, the furnace temperature of 475°C is chosen. To reduce the frequencies of nitric acid moistening and the amount of nitric acid used, the ashing aid is added to the carbonized rice samples obtained by overnight dry ashing without any ashing aid. In views of difficulty of rice ashing, cadmium content of common rice samples and interference with cadmium extraction (see below), the amount of sample ashed at once in one crucible is standardized to 20 g. The amount of sodium sulfate which is added to 20 g of rice sample is decided to be 1 m*l* of 10% solution, i. e. 0.1 g. This is about twice of the minimum requirement which has been estimated by a preliminary experiment.

Thus, the applicable ashing method is as follows:

1) Weigh 20 g of rice sample into ceramic crucible.

2) Ash overnight in the electric muffle furnace set at 475°C with an automatic temperature regulator.

3) Take out the crucible, cool, and add 1 m*l* of 10% solution of sodium sulfate and 1 m*l* of concentrated nitric acid. And, to increase the effect of these reagents by sufficient contact, crush carbonized sample with a glass rod.

4) After rinsing down a small amount of carbonized sample stainning on the glass rod with a small amount of water, heat gently on a sand bath until nitric fumes disappear.

5) Put in the furnace set at 350 to 400°C for 10 to 20 minutes.

6) Take out the crucible, cool, and moisten with concentrated nitric acid, and again heat gently on a sand bath until nitric fumes disappear. Put in the furnace set at 350 to 400°C.

7) Repeat the process of nitric acid moistening followed by furnace ashing until the carbon-free ash is obtained.

Through the above process, the carbon-free ash, pinkish colored, is obtained from polished rice within 2.5 m*l* volume of concentrated nitric acid. And the

greater part of the carbon free ash obtained is soluble in a warm dilute solution of nitric acid, only a little residue, in which a very small amount of cadmium is found by spectrography, remaining undissolved. Consequently, all the contents of the crucible is transfered into the separatory funnel, and extracted with dithizone. But, the small amount of residue does not interfere with cadmium extraction, and the erratic low result is not observed because of the negligibly low contnnt of cadmium in this residue. This is also proved by the recovey test which is shown in Table 7.

TABLE 1. Comparison of analytical results of cadmium obtained by dry ashing and wet digestion

Samples	Cadmium content	
	Dry ashing	Wet digestion
1	1018μg/kg	1027μg/kg
2	439	430

These samples are obtained from mine affected area in Toyama Prefecture. Variety name of sample 1 is 'Taisho-mochi' (Waxy rice), the other is 'Kurobe 1' (Nonglutinous rice).

As shown in Table 1, the dry ashing procedure above described is compared with wet digestion, using the samples of high cadmium content. It is considered that the result by this dry method is satisfactory, because the both results are nearly equal.

2. *Experiment on Interference in Colorimetric Microdetermination of Cadmium with Dithizone*

From the above mentioned advantages, the method of Saltzman was adopted for cadmium determination of rice samples, But, magnesium and some other metals interfered frequently with the extraction of cadmium. An experiment was made for the purpose of overcoming this difficulty.

Appearance and Cause of the Interference

This interference was discovered from the unreasonable result that the cadmium content of unpolished rice was extermely low in comparison with that of polished rice Subsequently, the following phenomena were gradually clarified: Color of aqueous layer at the end of the first extraction stage was deep red in the interfering case, while the color was orange in the normal case. The interference was observed more frequently when large quantities, about 50 g or more, of samples were used, than in the case of using a small amount of samples.

Appearance of the interference: To gain a better understanding for the interference, the method of Saltzman is outlined as follows:

1) Extract all cadmium together with a small amount of impurities such as zinc, lead, etc., from the sample solution, strongly alkalized, by the use of a

fairly strong dithizone-chloroform solution. (First extraction stage)

2) Back extract cadmium with a tartric acid solution removing a part of zinc. (Stripping stage)

3) Extract pure cadmium from the tartric acid solution with a very weak dithizone-chloroform solution by the procedure similar to the first extraction. (Second extraction stage) And measure the extinction of cadmium dithizonate comparing with the standard extinction.

In these processes, it was found that the interference originated in the first extraction stage. Hence, the detailed procedure of the first extraction stage shall be described here.

1) Dissolve ashed sample in a warm dilute solution of nitric acid. Transfer the solution into separatory funnel. Adjust the reaction to yellow range of thymol blue indicator (pH 3 to 8). Make up the volume to 25 m*l*.

2) Add 1 m*l* of 25%(w/v) solution of sodium-potassium tartrate, and mix.

3) Add 5 m*l* of 40%(w/v) solution of sodium hydroxide containing 0.05% of potassium cyanide, and mix.

4) Add 1 m*l* of 20%(w/v) solution of hydroxilamine hydrochloride solution, and mix.

Up to the above process, the external appearance is not distinguished between the interfering case and the normal case.

5) Shake for 1 minute exactly with a shaking machine. Transfer the chloroform layer to the second separatory funnel containing 25 m*l* of 2.5% (w/v) cold tartric acid solution.

In the interfering case, the alkaline aqueous solution, which is orange in the normal case or colorless in case of high cadmium sample, i. e. dithizone insufficient, turns deep red at this stage. And, metal dithizonates extracted in chloroform layer are rather little as compared with that of deep red aqueous layer.

7) Shake the first separatory funnel for 1 minute, after the addition of 10 m*l* of chloroform.

8) Transfer the chloroform rinsings into the second separatory funnel.

Thus, the metal dithizonates extracted into chloroform layer by the above rinsing process are rather little in the interfering case, and colorless rinsings are frequently obtained in spite of the deep red coloration of aqueous layer.

In this occasion, if the strong dithizone solution (nearly 0.1%) is used for the complete extraction of cadmium, a large amount of common interfering metals, mainly zinc and lead, are extracted into chloroform layer. These metals cause an erratic high result. But, the red color still remains in the aqueous layer. In a word, the frequent repetitions of this rinsing process are nearly unavairable for the complete removal of the deep red color of the aqueous layer. And, if the subsequent analytical procedures, the stripping and second extraction steps, are made with the above chloroform layer, the low analytical result is erratically obtained. Accordingly, it can be considered that cadmium in aqueous layer is

insufficiently extracted into chloroform layer, and a considerable amount remains in the aqueous layer together with red dithizonates which seems to consist mainly zinc and lead dithizonate.

The special feature of this interference is summarized as follows: The aqueous layer which is orange or colorless in the normal case turns red at the end of the first extractin stage. The color of chloroform rinsings which are pink in normal case is liable to fade. And, the analytical result is unreasonably lowered.

Cause of the Interference: On purpose to find what element interferes with cadmium extraction, an experiment was made on nearly all the elements which constitute rice ash. The results are presented in Table 2. Amount of

TABLE 2. Effect of main inorganic elements of rice ash on the interference

Elements (ion)	Content in 20 g of rice (mg)*		Elements added (mg)	Cd*** found (μg)	Color of aqueous layer
	Unpolished	Polished**			
$P(PO_4^{3-})$	61	32	75(P)+100(K)	1.94	Orange
K^+	30	17			
Mg^{2+}	10	3.3	50	1.39	Red
Ca^{2+}	3.0	1.0	30	1.95	Orange
Fe^{3+}	0.35	0.13	4	2.01	Orange
Al^{3+}	—	—	20	1.96	Orange
Mn^{2+}	0.60	0.35	5	2.07	Black
Cu^{2+}	0.07	0.04	0.5	1.94	Orange
Zn^{2+}	—	—	0.2	2.12	Orange
Pb^{2+}	—	—	0.1	1.95	Orange

* Data is calculated from the analytical results of 'Takeda-Wase' by Katakura and Hatanaka.
** Polishing rate of this rice is 10%.
*** In each case, 2 μg of cadmium is added.

metals used in this experiment was three to ten times of those expected in 20 g of unpolished rice. (The contents of elements in rice were quoted from the results of Katakura and Hatanaka.)

From the result of this experiment, it may be assumed that the interference is caused mainly by the presence of magnesium. But, the color tone of this red aqueous layer is fairly different from that observed in case of the practical samples. And, judging from the analytical result, it seems that the strength of the interference is smaller than in case of the practical samples.

Hence, the experiment on the interaction among zinc, lead, copper, manganese and magnesium was undertaken.

The result shown in Table 3 indicates that the interference of magnesium is intensified by the co-presence of zinc and lead.

Meanwhile, another experiment was made on the solution nearly free from zinc and lead. The result shown in Table 3** indicates that the interference

TABLE 3. Interference of zinc and lead in addition to magnesium

Elements added (mg)			Cd found*	Color of aqueous
Mg	Zn	Pb	(μg)	layer
0	1.0	0.5	2.20	Orange
10	0	0	1.72	Red
10	0	0	1.89**	Red
10	1.0	0	1.36	Red
10	0	0.5	1.20	Red
10	1.0	0.5	0.74	Red
10	1.0	0.5	0.80***	Black

* In each case, 2μg of cadmium is added.

** Zinc, lead, etc. are removed by the preliminary extraction with dithizone at pH about 9.0. The regular analytical procedure is made on its aqueous layer.

*** Manganese (1.0 mg, Mn^{2+} or MnO_4^-) and copper (0.25 mg, Cu^{2+}) are added in addition to the above three elements. In this case, valency of manganese has no relation to the appearance and the analytical results.

becomes considerably smaller than in the case of the sample containing zinc and lead, regardless of still remaining red color in aqueous layer.

It is likely that the red color of the aqueous layer and the slight interference observed in this experiment are caused by a very small amount of zinc and lead which are present as impurities in sodium hydroxide solution and dithizone-chloroform solution. From this, it can be generally said that the red coloration of the aqueous layer indicates the presence of the interference, regardless of its strength.

From above results, it seems that the strength of the interference is affected not only by the concentration of magnesium but also by that of zinc or lead. Zinc or lead in natural samples not to speak rice samples may be present in an amount larger than that of cadmium. But, these metals can hardly be removed from sample solution and reagents without any loss of cadmium. For this reason, it is considered, from the analytical view point, that the content of magnesium is a primary interfering factor.

In conclusion, it is comfirmed that the presence of a considerable amount of magnesium and a small amount of zinc and lead interferes with cadmium extraction. And, the red coloration of the aqueous layer is caused by the presence of the dithizonates of these metals.

Experiment on Preventive Way for the Interference

Although any white precipitate is invisible even when the sample solution is strongly alkalized, magnesium seems to interfere as magnesium hydroxide in the cadmium extraction. An experiment was therfore made on the amount of sodium-potassium tartrate which had been decided by Saltzman to be 1 m*l* of 25% (w/v) solution for normal samples.

TABLE 4. Effect of sodium-potassium tartrate on the interferference

Na-K tartrate solution used (25 g/100m*l*) (m*l*)	Cd found (μg)
1	0.27
2	0
4	0
6	0
10	2.08
15	2.10
10	1.98*

Magnesium (50 mg), cadmium (2 μg) and zinc (0.5 mg, as an interference accelerator) are added in every case.

* Preliminary extraction is made for the separation of magnesium using 10 m*l* of Na-K tartrate solution. The regular analytical procedure is applied for back extracted solution using 1 m*l* of Na-K tartrate solution.

As shown in Table 4, it is clarified that the interference can easily be prevented by the addition of 10 m*l* of 25% solution of sodium-potassium tartrate for 50 mg of magnesium. And, the analytical result obtained by adding in this amount is satisfactory as compared with the case* where the preliminary separation of magnesium and cadmium is made before the first extraction.

TABLE 5. Effect of sodium-potassium tartrate in the practical case

Na-K tartrate solution used (25%, m*l*)	Analytical result of Cd (μg/kg)	Color of aqueous layer
1	356*	Red (Red precipitate is formed.)
2	199	Red (Clear)
3	374	Red (week)
4	385	Orange
6	399	Orange
10	399	Orange
15	387	Orange
10**	398	Orange

The sample is obtained from a mine poisoned area in Toyama Prefecture. It is rich in cadmium. And the interference is severe. Determination is made on 8 g of polished rice. The results are represented as the content.

* As can also be seen from Table 4, the reason why 2 m*l* of the tartrate solution added brings about a bad result as compared with 1 m*l* of the solution added is unknown. As for the external appearance, only red precipitate is formed in case of 1 m*l*, in spite of no precipitate in case of 2 m*l*.

** Magnesium is separated by the preliminary extraction under the same conditions as the first extraction, but the tartrate solution is increased to 10 m*l*. The regular first extraction is made on its back extracted solution using 1 m*l* of the tartrate solution.

Furthermore, an experiment similar to that described in Table 4 was made on the polished rice sample in which the interference occurs easily. As shown in

Table 5, the result that the interference can easily be prevented by the sufficient addition of sodium-potassium tartrate is obtained.

Meanwhile, the limit concentrations of magnesium were estimated for 1 m*l* and 5 m*l* of 25% of the tartrate solution.

TABLE 6. Limit amount of magnesium for 1 m*l* and 5 m*l* of the tartrate solution

Na-Ktartrate solution used (25%, m*l*)	Mg added (mg)	Cd found (μg)
1	0	1.95
1	1	2.10
1	3	1.68
1	6	1.76
5	10	2.18
5	20	1.98
5	30	1.98
5	40	1.86*

In each case, 2 μg of cadmium is added.
* Slightly interfered.

As indicated in Table 6, it is ascertained that the limit amount of magnesium is roughly 2 mg for 1 m*l* of the tartrate solution and 40 mg for 5 m*l* of the tartrate solution. Accordingly, by the addition of 5 m*l* of the tartrate solution, magnesium content can be increased to about twenty times of the amount in the original method.

The above result is very interesting as compared with the following observation: Even 1 m*l* of 25% of the tartrate solution has such a great capacity that the formation of visible precipitate of magnesium hydroxide is completely prevented for 30 mg of magnesium in about 30 m*l* of alkaline aqueous solution, but this amount of tartrate allows the formation of a faint white turbidity for 40 mg of magnesium in the same solutlon as the above. Additionally, the composition of 30 m*l* of this alkaline aqueous solution is equal to the alkaline aqueous solution in the extraction steps of Saltzman's method.

From the above experiment, it is concluded that most of the rice samples (20g) can easily be determined without any interference by the increase of the amount of the sodium-potassium tartrate solution from 1 m*l* of the original method to 5 m*l*.

Thus, the recovery was measured by this improved method. As indicated in Table 7, a good result was obtained.

By this improved method, cadmium of about 250 samples of polished rice was determined in the previous study (Moritsugu and Kobayashi). In that occasion, there were observed no interference except for a small number of the rice samles obtained from mine poisoned district.

TABLE 7. Cadmium recovery by the improved method

Cadmium added (μg)	Cadmium found (μg)	Recovery (%)
0	0.74	—
1.0	1.74	100
2.0	2.63	96
3.0	3.73	100
4.0	4.67	99

The sample rice is obtained from Okayama Prefecture (low cadmium). A dilute solution of cadmium chloride is added to 20 g of polished rice before the dry ashing.

Consequently, in case of cadmium determination by the method of Saltzman, we must take care of the magnesium content of samples. And, whenever the aqueous layer turns red at the end of the first extraction stage, we must prevent the interference, decreasing the amount of sample or increasing the amount of sodium-potassium tartrate. Especially, the increase of the tartrate solution is effective, even when the precipitate of hydroxide of alkali earth is invisible in the sample solution strongly alkalized.

As for the increase of the amount of sodium-potassium tartrate for this colorimetric method, it has been reported that the analytical result is not affected even when its amount is increased to 40 ml of 20 % solution, whenever the pH value of the alkalized solution is kept at 11 by the addition of sodium hydroxide (Hashimoto and Tanaka 1959).

Accordingly, it can be concluded that the super-excessive addition of sodium-potassium tartrate is the one and only effective way to obtain a satisfactory result in the cadmium determination of the samples which contain a large amount of magnesium as compared with a very small amount of cadmium, unless the preliminary separation of magnesium and cadmium is made.

SUMMARY

Experiments were made on the ashing method of rice samples for cadmium determination and on the applicability of Saltzman's method for rice samples.

1) As for the ashing of rice samples, it is confirmed that dry ashing method can be recomended for the microdetermination of cadmium, provided that the furnace temperature is strictly controlled and sodium sulfate is used as an ashing aid.

2) The dry ashing of rice samples is considerably difficult. And the process of nitric acid moistening is essential in this case. But, if a small amount of sodium sulfate is used as an ashing aid, a rather rapid oxidation can be achieved without any erratic effect on the analytical results.

3) As the result of measurement of the ashing sample temperature, it is ascertained that the temperature of ashing sample is considerably elevated in early

stages of ashing. And, it seems that the elevation of sample temperature of a certain sample which can be easily ashed is proportional to its easiness of ashing.

4) For the cadmium determination of rice samples, the dithizone method of Saltzman is adopted, having a many advantages. But, the method has a weak point. Namely, the analytical result obtained by the method is frequently low in a considerable degree.

5) The process of Saltzman's method consists of three stages, i. e. the first extraction stage in which all cadmium is extracted from sample solution with a small amount of impurities into chloroform layer, the stripping stage where cadmium is back extracted with tartric acid, and the second extraction stage where pure cadmium is extracted with a weak dithizone-chloroform solution. It is clarified that the interference originates in the first extraction stage.

6) The special feature of the interference is red coloration of alkaline aqueous layer at the end of the first extraction stage. The color is orange or colorless in the normal case. It is concluded that the red coloration of aqueous layer indicates the presence of the interference in cadmium extraction, regardless of its strength or degree.

7) It is clarified that the interference is caused by the presence of a considerable amount of magnesium and a small amount of zinc and lead which are naturally found in the common rice samples of Japan. And, strength of the interference varies according to magnesium content and zinc or lead content in the sample. But, there is no question on the fact that the magnesium concentration in the sample solution is a primary interfering factor for the practical samples which may contain a considerable amount of zinc and lead as compared with cadmium.

8) As for the external appearance, it is observed that the interference occurs without any visible precipitate of alkali earth hydroxide in the alkalized sample solution. Namely, any visible difference can not be seen between the interfering case and the normal case until the aqueous layer turns red.

9) It is concluded that the interference is prevented by the increase of the amount of sodium-potassium tartrate, by the decrease of the concentration of magnesium in the sample solution by reducing sample weight, or, if we bear troubles, by the preliminary separation of cadmium and magnesium before the first extraction.

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